Glass formation from iron-rich phosphate melts

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\textbf{Abstract}

Iron-rich phosphate glasses with nominal Fe/P atom ratios between 1.0 and 1.6 were prepared by a roller-quenching technique. The critical cooling rates (CCR) for glass formation were estimated by differential thermal analysis and found to be in the range of \(10^2\)–\(10^4\) °C/s for the iron-rich melts, compared to \(1\)–\(10^3\) °C/s for conventional iron phosphate melts with Fe/P ratios near 0.50. The Fe(II)/Fetotal fraction in the quenched glasses increases with melt time and temperature, and ranges between 0.30 and 0.55 for the glasses studied. Raman spectroscopy indicates that the structures of the iron-rich phosphate glasses are based on isolated orthophosphate tetrahedra, similar to what are found in \(\alpha\)-FePO\(_4\).

1. Introduction

Iron phosphate glasses have been developed as alternative materials for high-level nuclear waste encapsulation [1–8]. The glasses can dissolve large quantities of a variety of waste components while retaining outstanding chemical durability. Iron phosphate glasses also exhibit interesting electrical and magnetic properties that depend on the iron coordination number and redox state [9,10].

Iron phosphate compositions with nominal Fe/P atom ratios between 0.33 and 0.67 have good glass forming ability (GFA) and have been widely studied [1–8]. Phosphate-rich ferrous ultraphosphate glasses (FeO/P\(_2\)O\(_5\) < 1:1) were made in sealed silica tubes under vacuum and their structures and properties characterized [11,12]. Glasses with Fe/P ratios as high as 1.83 have been prepared by quenching microwave- or joule-heated melts between pre-cooled copper plates [13], but the structure and properties of these iron-rich glasses were not investigated. Glasses with Fe/P ratios between 1.0 and 2.3 were made by twin-roller-quenching [14], and the magnetic properties of one glass (Fe/P = 2.3) were reported. However, little is known about the structure and thermal stability of iron-rich (Fe/P > 1) phosphate glasses.

The structures of iron phosphate glasses with Fe/P ratios between 0.33 and 0.67 are reported to be similar to the short range structure of crystalline Fe\(_3\)(P\(_2\)O\(_7\))\(_2\) [7]. Ferrous and ferric ions in distorted octahedral sites are assumed to link neighboring pyrophosphate anions to constitute the glass structure. The fraction of ferrous ions, Fe\(^{2+}\)/Fetotal, in the quenched glasses increases with melting temperature and with iron content. For conventional iron phosphate glasses, Fe\(^{2+}\)/Fetotal is below 0.4 and melts with Fe\(^{2+}\)/Fetotal ≥ 0.4 crystallize more rapidly when quenched in air by pouring into steel molds [7].

It is well-known that GFA is enhanced for melt compositions near deep eutectics [15–17]. GFA can be characterized using critical cooling rate (CCR) experiments to determine the conditions required to avoid crystallization upon quenching. Turnbull proposed that GFA was related to the ratio between the glass transition temperature \((T_g)\) and the liquidus temperature \((T_L)\); the greater \(T_g/T_L\), the better the GFA [18]. Other common glass stability (GS) parameters are listed in Table 1. These GS parameters were evaluated by Nascimento, et al. [23] using thermal analytical information and related to GFA for eight different glass forming systems. The three GS parameters listed in Table 1 correlate well with experimental measurements of GFA, and their respective critical cooling rate relationships are also given in Table 1.

The liquidus surface of the Fe\(_3\)PO\(_4\)–FePO\(_4\) system was reported by Wentrup [24] to have a eutectic point at Fe/P = 1.38 (molar). This system has been re-investigated as part of a larger study of the FeO–P\(_2\)O\(_5\) liquidus surface that is to be published elsewhere [25]; a similar eutectic composition was found, but at a greater eutectic temperature (1070 °C vs. 968 °C) than reported by Wentrup.

In the present study, the glass forming tendencies of iron phosphate melts with initial molar compositions around the reported eutectic point of the Fe\(_3\)PO\(_4\)–FePO\(_4\) system (1.00 ≥ Fe/P ≥ 1.60) were investigated. The melts studied here have significantly greater iron contents than typical iron phosphate glasses, and Raman spectroscopy indicates that these glasses possess “inert” structures [26] based on isolated orthophosphate tetrahedra linked through iron polyhedra. The glass forming ability of these melts was studied using DTA characterization and the GS parameters in Table 1.
2. Experimental procedures

Compositions near the eutectic point between FePO$_4$ and Fe$_3$PO$_7$, with nominal Fe/P atom ratios between 1.0 and 1.6, were investigated, along with compositions of conventional iron phosphate glass (Fe/P $\geq$ 0.5, 0.67 and 0.82). Mixtures of reagent grade Fe$_2$O$_3$ (Alfa Aesar, $\geq$45 µm, $\geq$99%) and FePO$_4$, obtained by dehydrating FePO$_4$$\cdot$H$_2$O ($\geq$99%, Alfa Aesar), weighing 2–5 grams were used to prepare the iron-rich (Fe/P $\geq$ 1.0) phosphate glasses. Mixtures of NH$_4$H$_2$PO$_4$ (Alfa Aesar, 98%) and Fe$_3$O$_4$ were used to prepare 10–30 g of the conventional (Fe/P $<$ 1.0) iron phosphate glasses. For all glasses, the raw materials were thoroughly mixed and then heated in alumina crucibles for the times and temperatures indicated in Table 2. Melted were quenched either by cooling thick (2–4 mm) pattiess in air, by pressing thin (~1 mm) samples between steel plates, or by preparing very thin (~100 µm) ribbons with a twin-roller quencher. The distance between the two rollers and the rotation rate could be adjusted to modify the ribbon thickness, and thus the quench rate.

The quenched samples were pulverized to <53 µm and analyzed by X-ray diffraction (XRD Scintag XDS 2000) and differential thermal analysis (Perkin-Elmer DTA7). The DTA runs were performed in air at a heating rate of 10 °C/min. Characteristic temperatures from the DTA experiments were used to calculate CCRs based on the equations reported by Nascimento, et al. [23] and summarized in Table 1.

The melting times and temperatures were varied for some samples to study processing effects on the Fe$^{2+}$/Fe$_{total}$ ratio. The Fe$^{2+}$/Fe$_{total}$ ratios in the glasses were determined by a titration method [27] with 2 mM KMnO$_4$. Raman spectra (Horiba-Jobin Yvon LabRam-HR) in the range of 50–2000 cm$^{-1}$ were collected using a He–Ne laser (632.8 nm) on glass powders and on powders of crystalline α-FePO$_4$ and Fe$_5$(P$_2$O$_7$)$_2$. Powders from roller-queched iron-rich (Fe/P $\geq$1) glasses were analyzed, along with powders from plate-queched conventional (Fe/P $<$ 1) glasses. α-FePO$_4$ was prepared by dehydrating FePO$_4$$\cdot$H$_2$O at 880 °C for ~24 h. Fe$_5$(P$_2$O$_7$)$_2$ was prepared by heating stoichiometric mixtures of Fe$_3$(P$_2$O$_7$)$_3$ and Fe$_2$P$_2$O$_7$ in sealed silica tubes for 12 h at 900 °C. Fe$_3$(P$_2$O$_7$)$_3$ was initially prepared using methods reported in [28], and Fe$_2$P$_2$O$_7$ was prepared by reducing FePO$_4$ in forming gas (10% H$_2$ and 90% Ar) at 560 °C.

### Table 1

GS parameters and calculation equation.

<table>
<thead>
<tr>
<th>GS parameter</th>
<th>Reference</th>
<th>Equation for critical cooling rate (°C/s), from ref. [23]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$K_t$ = $\frac{T_g}{T_L}$</td>
<td>[18]</td>
<td>$-1$</td>
</tr>
<tr>
<td>$K_i$ = $\frac{T_p}{T_L}$</td>
<td>[19,20]</td>
<td>CCR = 16.7–33.1 $K_s$</td>
</tr>
<tr>
<td>$K_w$ = $\frac{T_L – T_p}{T_L}$</td>
<td>[21]</td>
<td>CCR = 4.0–20.5 $K_w$</td>
</tr>
<tr>
<td>$K_h$ = $\frac{T_L – T_m}{T_L}$</td>
<td>[22]</td>
<td>CCR = 3.0–2.44 $K_h$</td>
</tr>
</tbody>
</table>

$T_g$ is the glass transition temperature, $T_L$ is the melt liquidus temperature, and $T_p$ is the peak temperature for crystallization. All temperatures are in Kelvin.

### 3. Results

#### 3.1. Glass forming tendency

Fig. 1 shows the XRD patterns of glasses from (a) a roller-queched Fe/P = 1.30 melt and (b) the same melt after quenching between steel plates. The broad diffuse peak in the pattern for the roller-queched sample indicates the amorphous state of the sample. The crystalline phases detected in this partially crystallized, plate-queched sample are FePO$_4$, Fe$_5$(P$_2$O$_7$)$_2$ and Fe$_3$(PO$_4$)$_6$.

Table 3 summarizes the XRD analyses of glasses prepared from melts with different nominal compositions and quenched by different means. Every sample prepared from the iron-rich melts (Fe/P $\geq$1.0) exhibited evidence of crystallization when cooled in air or between steel plates. However, the roller-queched melts yielded glasses with no detectable crystallinity. The cooling rates that each method can achieve depend on the melt temperature, sample size and other experimental conditions. From reports in the literature, cooling in air from temperatures below 1300 °C and pressing from 1300 °C between steel plates can achieve cooling rates in the range of $10^{-6}$ °C/s [23,29]. Twin-roller-queching can achieve cooling rates as high as $10^{-3}$ °C/s [30].

#### 3.2. The dependence of Fe(II) content on melt conditions

Fig. 2 shows that the relative Fe(II) content of roller-queched, iron-rich glasses increases with melt time, reaching a constant value after about 1 h. Fig. 3 shows that the Fe(II) content increases with melt temperature, and that glasses with greater Fe/P ratios have greater Fe(II) contents when quenched from melts held at the same temperature. A model to predict the effects of melt composition, atmosphere and temperature on the equilibrium Fe$^{2+}$/Fe$_{total}$ ratio has been developed and will be reported elsewhere [31].

#### 3.3. Thermal characteristics

Fig. 4 shows DTA patterns collected in air for several glasses (melting time: 2 h) investigated in this work. In general, for glasses melted under similar conditions, $T_g$ increases and the peak temperature for crystallization ($T^+_C$) decreases with increasing Fe/P ratio, as summarized in Fig. 5. (Note that the characteristic temperatures for the iron-rich glasses were obtained from roller-queched samples, whereas plate-queched samples of the conventional iron phosphate glasses were evaluated.) The estimated uncertainty of these

### Table 2

Glass compositions and the melting conditions.

<table>
<thead>
<tr>
<th>Initial Fe/P ratio</th>
<th>Melting temperature (°C)</th>
<th>Melting time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.60</td>
<td>1250</td>
<td>2</td>
</tr>
<tr>
<td>1.50</td>
<td>1200</td>
<td>2</td>
</tr>
<tr>
<td>1.38</td>
<td>1150</td>
<td>0.5, 1.0, 2.0, 6.0</td>
</tr>
<tr>
<td>1.38</td>
<td>1200</td>
<td>0.5, 2</td>
</tr>
<tr>
<td>1.30</td>
<td>1200</td>
<td>2</td>
</tr>
<tr>
<td>1.00</td>
<td>1250</td>
<td>2</td>
</tr>
<tr>
<td>1.00</td>
<td>1300</td>
<td>0.5, 1.0, 2.0, 6.0</td>
</tr>
<tr>
<td>0.82</td>
<td>1200</td>
<td>2</td>
</tr>
<tr>
<td>0.67</td>
<td>1200</td>
<td>2</td>
</tr>
<tr>
<td>0.50</td>
<td>1200</td>
<td>2</td>
</tr>
</tbody>
</table>

Fig. 1. XRD patterns from samples quenched from melts with a nominal Fe/P = 1.30, held for 2 h at 1200 °C, then a) roller-queched, or b) quenched between steel plates.
temperatures is ±5 °C based on the multiple DTA runs. Also shown in Fig. 5 are the liquidus temperatures ($T_L$) for the respective melts, as reported elsewhere [25]. The values of ($T_P$ - $T_g$) for the iron-rich (Fe/P ≥ 1.0) glasses are much smaller (35–67 °C) than that (∼300 °C) of the conventional iron phosphate glass (Fe/P = 0.50). This is consistent with the much better glass forming tendency of the latter composition, as indicated by the XRD results summarized in Table 3. Moguš-Milanković, et al. [32] report a similar decrease in ($T_P$ - $T_g$) with increasing Fe/P content for a much smaller range of iron phosphate glass compositions.

### 3.4. Glass structure

Raman spectra collected from plate-quenched glasses with nominal Fe/P ratios less than 1.0 are compared with that collected from crystalline Fe$_2$(P$_2$O$_7$)$_2$ in Fig. 6. For Fe$_2$(P$_2$O$_7$)$_2$, peaks in the range of 1000–1200 cm$^{-1}$ can be assigned to symmetric and asymmetric stretching modes of P–O bonds in the pyrophosphate anions [33]. The low intensity peak near 760 cm$^{-1}$ is assigned to a P–O–P stretching mode, the peak near 670 cm$^{-1}$ is assigned to a P–O bending mode, and the series of peaks below 400 cm$^{-1}$ are assigned to various Fe–O and P–O modes. The Raman spectra from the iron phosphate glasses have a broad peak centered near 1030–1050 cm$^{-1}$, several low intensity peaks below 600 cm$^{-1}$, and, for the glasses with Fe/P = 0.50 and 0.67, a less intense peak between 690 and 800 cm$^{-1}$. The broad peak centered near 1030–1050 cm$^{-1}$ has been assigned to the symmetric and asymmetric stretching modes of non-bridging oxygens associated with different phosphate tetrahedra; for example, non-bridging oxygens on tetrahedra with one bridging oxygen ($Q^1$ tetrahedra) account for peaks near 1030–1050 cm$^{-1}$ and those on tetrahedra with two bridging oxygens ($Q^2$) account for shoulders near 1200 cm$^{-1}$ [34,35]. The peak between 600 and 800 cm$^{-1}$ is assigned to the symmetric stretching mode of bridging oxygens, (P–O–P)$_{sym}$, in the glass structure [36]. The similarity in the spectra from these glasses with that from crystalline Fe$_4$(P$_2$O$_7$)$_2$ is consistent with the proposal that these glasses possess short range structures that are similar to the short range structure of crystalline Fe$_4$(P$_2$O$_7$)$_2$ [7]. In particular, these glasses possess pyrophosphate anions that are linked by ferrous and ferric polyhedra.

Raman spectra collected from roller-quenched iron-rich glasses (Fe/P ≥ 1.00) are shown in Fig. 7, and are compared with that collected from crystalline $\alpha$-FePO$_4$. The Raman spectra from the iron-rich glasses are distinctly different from those of the conventional iron phosphate glasses, shown in Fig. 6. The spectra from the iron-rich glasses are dominated by an intense peak centered near 1002 cm$^{-1}$, as well as a number of lower intensity peaks in the range between 100 and 500 cm$^{-1}$. The peak centered near 1002 cm$^{-1}$ is assigned to P–O stretching modes of non-bridging oxygens on $Q^1$ tetrahedra, consistent with the spectrum from $\alpha$-FePO$_4$ where this peak is found at 1009 cm$^{-1}$. This peak is broader (full width at half-maximum = 30–50 cm$^{-1}$) in the spectra from the glasses than that...
obtained from $\alpha$-FePO$_4$ (FWHM=10 cm$^{-1}$), consistent with a
greater degree of disorder associated with these roller-quenched
glasses. (The glass with Fe/P=1.6 fluoresced substantially when the
Raman spectra were collected. This might contribute to the relative
broadening of the 1000 cm$^{-1}$ peak noted for this sample in Fig. 7.)
The broadening and decrease in frequency of this peak for the glasses,
compared to $\alpha$-FePO$_4$, is consistent with what was reported by Burba,
et al. [37] in their recent study of crystalline and disordered $\alpha$-FePO$_4$.
There is no distinct evidence for non-bridging oxygen modes at
greater wave numbers in the Raman spectra of the iron-rich glasses,
nor for the (P–O–P)$_{sym}$ stretching mode near 700 cm$^{-1}$. The peaks
between 400 and 500 cm$^{-1}$ arise from the O–P–O bending modes of
$Q^0$ units [32,38]. The peaks at ~260 cm$^{-1}$ are likely related to the
bending $Q^0$ with Fe as modifier [38]. The peaks below 200 cm$^{-1}$ have
been assigned to both P–O and Fe–O modes [39,40]. The similarity in
the spectra from the iron-rich glasses with the spectrum from $\alpha$-
FePO$_4$ in Fig. 7 indicates that similar P- and Fe-tetrahedra likely exist
in the glasses.

4. Discussion

4.1. Glass formation and structure

Fig. 8 compares the glass forming range (region “a”) for conven-
tional iron phosphate glasses based on the reported data [6,7,9], with
the glass forming range for the new iron-rich phosphate glasses studied
in this work (region “b”). Here, the open symbols represent the com-
positions of the glass batches and the “x” symbols within region “b”
indicate the compositions of the iron-rich, X-ray amorphous glasses
prepared by roller-quenching. The reduction of Fe$^{3+}$ to Fe$^{2+}$ during
melting decreases the O/P ratios of these quenched glasses from their
nominal values. The heavy line in Fig. 8 indicates compositions with an
O/P ratio of 4.0; compositions below this line have O/P < 4.0. The new
glass forming range (region “b”) for iron-rich compositions is bounded
by the crystalline phases FePO$_4$, Fe$_2$P$_2$O$_7$, Fe$_3$(P$_2$O$_7$)$_2$, Fe$_3$PO$_4$, and Fe$_7$
(PO$_4$)$_6$, each of which has been identified by XRD in various partially
crystallized samples (Table 3).
It is worth emphasizing that the reported glass forming range for the conventional iron phosphate glasses (region “a” in Fig. 8) represent lower quenching rates (as cast or plate quench) than are obtained by the roller quench techniques used to produce the iron-rich glasses (region “b”). It is expected that roller-quenching would increase substantially the glass forming range of meta- and polyphosphate compositions (3 ≤ O/P ≤ 4) beyond that indicated in “region a”. In the present work, only roller-quenched melts near the orthophosphate (O/P ≤ 4) composition were studied.

If the acidic phosphate units accept oxygens from the more basic iron oxide, then at O/P = 4, only non-bridging oxygens will be associated with the phosphate anions, forming isolated orthophosphate (Q^0) units that must be linked to neighboring iron polyhedra through the non-bridging oxygens. For glasses with O/P > 4, the additional oxygens must be incorporated into the structure in the form of Fe–O–Fe bonds, with little effect on the nature of the orthophosphate anions. (Similar “invert” structures have been reported for titanium-rich phosphate glasses [41].) The Raman spectra of the iron-rich glasses (Fig. 7) are dominated by a narrow peak at 1002 cm⁻¹ that indicates the presence of the expected orthophosphate units, and this peak does not change with increasing Fe/P (and O/P) ratio. In contrast, the broad Raman peak centered near 1050 cm⁻¹ in the spectrum of the Fe/P glass (Fig. 6) shifts to lower wavenumbers with increasing Fe/P ratio, consistent with the replacement of Q^1-tetrahedra by Q^0-tetrahedra as the overall O/P ratio increases. The Raman spectra indicate that the phosphate-rich compositions have larger phosphate anions that include Q^2 (middle units) and Q^1 (chain terminators) tetrahedra, whereas the iron-rich glasses possess only isolated (Q^0) tetrahedra. The relative complexity of the conventional glasses is reflected in the broader Raman peak associated with the P–O–P stretching modes (Fig. 6), compared to the respective peaks from the iron-rich glasses. A detailed description of the Raman spectra of iron phosphate compounds and glasses will be presented elsewhere [42].

4.2. Critical cooling rate estimation

Fig. 9 shows the calculated critical cooling rates (CCRs) for the iron phosphate melts based on the characteristic temperatures shown in Fig. 5 and the equations listed in Table 1. The CCRs for the iron-rich (Fe/P ≥ 1.0) phosphate melts are in the 10⁻³–10⁻⁴ °C/s range, compared to CCRs of 1–10 °C/s for conventional Fe–phosphate melts. The calculated CCRs indicate the difficulties of making iron-rich phosphate glass by quenching in air or pressing between metal plates. The tendency of CCR to increase with increasing Fe/P ratio is consistent with the glass forming experiments summarized in Table 3.

In general, phosphate glasses with longer phosphate chains (smaller O/P ratios) are more stable against devitrification. For example, Wange, et al. [43] report that crystallization tendency of a complex Ca-phosphate glass increases with increasing O/P ratio as smaller phosphate anions are available to constitute the glass structure. (Crystallization tendency also depends on the nature of oxides used to modify the glass; oxides that strengthen the glass network, like Al₂O₃ and TiO₂, increase viscosity and reduce crystallization tendency compared to oxides like CaO and Na₂O.) The addition of various oxides to an iron phosphate base glass tends to reduce the temperature difference between T_g and T_c, indicating an increase in crystallization tendency with increasing O/P ratio [8], although the extent of the temperature difference also depends on the nature of the oxide added. The enhanced crystallization behavior may be related to the changes in the rheological properties of phosphate glasses with shorter average phosphate chain-lengths. The rheological characteristics and the tendency of a phosphate melt to crystallize when sheared also depend on the type of phosphate anions that are present in the melt [44]. Smaller anions are often associated with faster crystallization.

The high CCR for glass formation from the iron-rich phosphate melts will limit the use of these glasses, particularly for applications like waste fixation that require the formation of relatively large samples with minimal crystallization. However, the expanded range of glass formation to the orthophosphate “invert” structures raises the likelihood that other compositions with similar structures can be developed, including those with a lower CCR. For example, the structures of the “NASICON” (sodium super-ionic conductors) family of glasses are based on orthophosphate ions and include ferric phosphate versions [45]. More recently, lithium-doped iron orthophosphate glasses have been produced in studies to develop cathode materials for Li-ion batteries [46]. The crystallization tendency of these glasses, determined by the difference in T_g and T_c obtained by DTA measurements, decreases with the addition of Li₂O.

5. Conclusion

Studies of glass formation and structure in the iron phosphate system have been extended to iron-rich compositions, with nominal Fe/P ratios in the range of 1.0–1.6. Critical cooling rates estimated from characteristic temperatures obtained by differential thermal analyses are at least 10³ times greater for the new iron-rich compositions than for the conventional iron phosphate melts. The fraction of Fe(II) increases with increasing melt temperature and time. These new glasses have structures based on isolated phosphate tetrahedra (Q^0) and on Fe(II) and Fe(III) polyhedra.

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